

PTO 10-4767

WO  
20020214  
A2  
0212158

METHOD FOR CATALYTICALLY PRODUCING ORGANIC SUBSTANCES BY PARTIAL  
OXIDATION

[Verfahren zum katalytischen Erzeugen von organischen Stoffen durch partielle Oxidation]

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UNITED STATES PATENT AND TRADEMARK OFFICE  
WASHINGTON, D.C. JULY 2010  
TRANSLATED BY: THE MCELROY TRANSLATION COMPANY

PUBLICATION COUNTRY	(19):	WO	
DOCUMENT NUMBER	(10):	0212158	
PUBLICATION DATE	(43):	20020214	
APPLICATION NUMBER	(21):	PCT/EP01/08002	
APPLICATION DATE	(22):	20010711	
INTERNATIONAL CLASSIFICATION <sup>7</sup>	(51):	C 07 C	51/265
			51/25
			57/05
			63/16
			63/26
		B 01 J	8/04
			8/18
FILING LANGUAGE	(25):	German	
PUBLICATION LANGUAGE	(26):	German	
PRIORITY COUNTRY	(30):	DE	
PRIORITY NUMBER	(30):	100 38 755.1	
PRIORITY DATE	(30):	20000809	
PRIORITY COUNTRY	(30):	DE	
PRIORITY NUMBER	(30):	101 04 406.2	
PRIORITY DATE	(30):	20010201	
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DESIGNATED CONTRACTING			

STATES (national):	(81):	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
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#### DESIGNATED CONTRACTING

STATES (regional):	(84)	ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
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TITLE	(54):	METHOD FOR CATALYTICALLY PRODUCING ORGANIC SUBSTANCES BY PARTIAL OXIDATION
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FOREIGN TITLE	[54A]:	Verfahren zum katalytischen Erzeugen von organischen Stoffen durch partielle Oxidation
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The present invention relates to a method for catalytically producing organic substances by partial oxidation of an organic feedstock in the presence of molecular oxygen at temperatures in the range of 200-500°C in one or more series-connected reactors containing a catalyst for use in the production of a gaseous product mixture.

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The feedstock is converted into the final product in one or more oxidation steps, wherein, in each oxidation step, the individual molecules of the feedstock release one or more atoms of hydrogen and/or carbon and are also able to bind individual oxygen atoms. The released carbon combines with oxygen to form carbon dioxide and/or carbon monoxide, and the released hydrogen combines with oxygen to form water. As a rule, one fraction of the feedstock is completely oxidized to carbon dioxide and/or carbon monoxide; another fraction is converted into other organic substances. The oxygen required for the oxidation reaction is taken from the carrier gas (normally ambient air that has been pre-heated in a heat exchanger). Because of the various oxidation reactions, the entire method is highly exothermic.

According to the invention, e.g., phthalic anhydride, maleic anhydride is produced from butane or benzene, acrylic acid from propylene, acetic acid from C<sub>4</sub> hydrocarbons or anthraquinone.

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A typical product, which is produced worldwide in large quantities based on this principle, is phthalic anhydride (PA) from a feedstock mixture that contains orthoxylene or naphthalene and molecular oxygen in a concentration that is normally present in ambient air or that is increased by additional concentration. PA is produced at temperatures in a range from 200-500°C in a catalyst-containing reactor through which reactor a cooling fluid is passed and from which a product mixture containing gaseous PA vapor is withdrawn. This type of PA production will subsequently be described by way of an example for all organic products that can be produced by catalytic partial oxidation in the gas phase, with the possibility of also using a plurality of series-connected reactors.

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\* [Numbers in right margin indicate pagination of the original text.]

A method of this type with a multi-tube reactor is known from U.S. Patent No. 4,592,412. In this case, the reactor comprises a plurality of vertical tubes that contain the granular catalyst. The catalyst on the basis of vanadium pentoxide may also be composed of substrate elements that are coated with catalytic substance. A cooling fluid is passed along and around the outside of the many tubes that contain the catalyst in order to dissipate the heat that is released by the exothermic reaction. In the prior-art method, molten salt is preferably used as the cooling fluid, which, however, requires complex and therefore expensive apparatuses.

Apart from the high cost of investment, there are other reasons why a variety of problems are associated with the multi-tube reactor described above. Because of the heavy weight and the large dimensions of the reactor (150-250 metric tons and a diameter of 7-9 m alone for the bundle of tubes for conventional reactor sizes), cost-intensive special transports are required. Due to the fact that the starting material required for the production of the reactor is supplied in non-commercial dimensions and that the production is labor-intensive, the reactor delivery times are long. The random distribution of the catalyst in the individual tubes is responsible for a high loss of pressure on the gas side in conjunction with a high consumption of energy for the transport of the feed gas. In addition, this type of construction entails a number of other problems that are related to processing and reaction technology and that will be discussed in greater detail below.

To be highly selective and to achieve a long service life, modern high-performance catalysts require very uniform temperatures. The admissible temperature variation of the cooling fluid within the space surrounding the tubes is therefore extremely limited. In the prior-art method, this necessarily entails large recirculation flow rates of the cooling fluid in conjunction with a high energy requirement and high costs of investment for the recirculation pumps. /3

Typically, in all known oxidation methods in which a reactor with a stationarily incorporated catalyst (fixed bed) is used, the conversion of the feedstock into the end product and the related development of heat over the entire catalyst packing is very nonuniform, which is attributable to the fact that in the PA method, for example, more than 90% of the heat of reaction is produced on the inlet-side half of the catalyst packing (main reaction zone). In the reactor according to the prior-art method, reaction temperatures far above the temperature of the walls of the tube are obtained in the catalyst of the main reaction zone due to the poor heat transfer between the catalyst and the walls of the tube, whereas in the outlet-side half of the catalyst packing (secondary reaction zone), the reaction temperature is very close to that of the cooling fluid. In the inlet-side half of the catalyst, in most cases a so-called hot spot forms, the temperature of which can come close to the self-ignition temperature of the product. Thus, in the presence of minor variations in the reaction conditions, it is possible for the gas to ignite, which leads to partial or total damage to the catalyst due to overheating. In addition, at high temperatures in the catalyst, a feedback effect can accelerate the process of overheating since, as experience has shown, as the reaction temperature increases, the activity of the catalyst, and hence the quantity of oxidized feedstock, increases as well so that the generation of additional heat can easily have the effect that the self-ignition temperature of the gas is reached. Furthermore, as the activity increases, the selectivity of the catalyst decreases, i.e., the product yield decreases and more byproducts are formed.

For the economic production of PA, it is recommended that a reactor feed gas with a preferably very high concentration of feedstock substances be used. This makes it possible to use smaller and, as a result, less expensive apparatuses for plants with the same capacity. However, due to the above-described risk of an overreaction of the catalyst, the concentration in the prior-art method cannot be increased to the extent desirable to ensure economic production.

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The problem to be solved by the present invention is to improve the method mentioned above and to increase the product yield while improving the operational safety and ensuring a less expensive operation. The objective is to operate not only one reactor but a plurality of series-connected reactors in order to be able to expand, e.g., already existing plants.

According to the present invention, this is accomplished in that at least one reactor is a cooling tube-type reactor with cooling tubes, through which a cooling fluid flows, with 40-100 wt% of the total quantity of the catalyst being disposed in the form of a coating on the outside of the cooling tubes and with the feedstock mixture containing the feedstock and the molecular oxygen coming into contact with the catalyst layers. Part of the total quantity of catalyst may also be disposed on uncooled surfaces in the cooling tube-type reactor.

Another important aspect of the invention is that instead of the molten salt that is commonly used in the prior-art tubular reactor, a vaporizable liquid is used to dissipate the reaction heat in the cooling tube-type reactor, e.g., it is possible to use Diphyl as the cooling fluid. The focus of the subsequent discussion will be the production of PA, but the explanations apply by analogy to the production of other substances as well.

Preferably, at least half the cooling tubes in the cooling tube-type reactor are designed in the form of finned tubes with fins projecting on the outside, which fins are at least in part coated with the catalyst. By using finned tubes instead of smooth tubes, it is possible to considerably increase the catalytically active surface without increasing the diameter of the tubes or the number of tubes. It is recommended that at least 10 wt% of the total catalyst quantity be applied as coating to the fins. As a rule, the catalyst coatings have layer thicknesses in a range from 0.05-5 mm.

Coating the cooling tubes with the catalyst substance leads to an improved heat transfer from the catalyst onto and through the tube wall to the cooling fluid. In this manner it is possible to considerably reduce the high reaction temperatures that are unfavorable for the prior-art method in the main reaction zone of the cooling tube-type reactor. /5

Another advantage of the cooling tube-type reactor is that by using tubes that are finned on the outside, it is possible to efficiently increase the gas-side heat exchange surface into a multiple of the usual surface area of the reactors that are used in the prior-art method. By increasing the surface area, the heat of reaction can be dissipated more effectively and at a lower temperature gradient, which leads to an additional decrease of the reaction temperatures. By decreasing the reaction temperatures during oxidation reactions, it is generally possible to increase the selectivity of the catalyst and, as a result, the product yield. The operational safety is increased commensurately with the increase in the gap between catalyst temperature and self-ignition temperature of the gas.

Another important advantage of decreasing the reaction temperature as described in the two preceding paragraphs is that it is now possible to increase the concentration of the feedstock in the carrier gas far beyond the concentrations possible in the prior-art method without a risk of overreaction since the reaction temperature can be maintained at a sufficiently safe gap from the self-ignition temperature of the gas. In addition, the resulting reduction of the carrier gas quantity to be transported leads to energy savings for the operation of the carrier gas blower, for preheating the carrier gas and, when cooling the product mixture, to the separation of the product.

Additional energy savings result from the disclosed configuration of the catalyst substance on the surfaces of the fins of the cooling tubes. This leads to a considerable reduction of the gas-side pressure loss across the entire cooling tube-type reactor as compared to the principle of random charging with catalyst elements commonly used in the prior-art multi-tube reactor. In addition to the energy savings



described above, the cost of the blower and its associated drive required to transport the carrier gas is reduced as well; due to the lower delivery pressure, the blower can be designed more simply and produced less expensively, and due to the lower energy requirement, the dimensions of the drive can be reduced as well.

In the cooling tube-type reactor, it is possible to replace the old spent catalyst with a new catalyst in a shorter period of time than in the multi-tube reactor in which each separate tube must be individually filled with the highest accuracy. Because of the principle underlying the present invention, the individual bundles of tubes can be constructed so as to allow them to be pulled out of the reactor so that bundles of tubes containing the spent catalyst can be replaced with newly coated tube bundles in a manner that saves both time and cost. The removability of the bundles also makes it easier to remove the spent catalyst substance and to subsequently apply a new coating, which can be carried out without the need to shut down the reactor, for example, in the factory of the catalyst manufacturer. The bundles of tubes can be readily manufactured in a standard size, which makes it possible to re-use the newly coated bundles in a reactor of another plant operator. /6

In view of the high heat of reaction that is generated in the inlet portion of the reactor, it is very important for the economic efficiency of the method disclosed by the present invention to keep the number of cooling tubes at a minimum. To this end, it is possible to use, e.g., a material with a thermal conductivity higher than that of steel (e.g., copper) for the fins in the main reaction zone. As a result, it is possible to use relatively large fins of low thickness, so that the temperature differences between the fin edge and the core tube can be kept small.

However, in the secondary reaction zone of the cooling tube-type reactor, in which considerably less reaction heat is generated, steel fins in dimensions identical to those in the main reaction zone can be

used. This has the additional advantage that the geometrical relationships are identical in all parts of the reactor.

In addition to the dimensions and the material, the shape of the individual fin is also important as far as the heat transfer properties of a finned tube are concerned. A round fin, for example, ensures a more favorable temperature distribution than a fin with a square or rectangular shape. Therefore, this shape is especially well suited for zones of the reactor in which the thermal load is high. Fins with a square or rectangular shape, on the other hand, are able to accommodate larger heat exchange surfaces per unit volume. This is useful in zones with a low thermal load. When using rectangular fins, it may be useful to choose the fin length and width in a ratio of approximately 2:1 so that each fin can be connected to the two legs of the U-tube. In cases in which the thermal load is extremely high, a fin of variable thickness may also be useful, i.e., the thickness of the fin is highest near the core tube and steadily decreases towards the edge. /7

In particular, in the outlet region of the cooling tube-type reactor, it is not necessary at all points that the catalyst be intensively cooled by a cooling fluid. It can therefore be useful and cost-efficient for 5 to 40 wt% of the total catalyst quantity to be disposed on uncooled surfaces of metal or other suitable materials. In this context, it may be useful to alternately pass the reaction gas over uncooled and cooled catalytically coated surface areas.

One of the main advantages when using a vaporizable cooling fluid in the cooling tube-type reactor instead of the molten salt that is conventionally used in the prior-art multi-tube reactor is the uniform temperature that is only dependent on the pressure of the fluid while, at the same time, having a better heat transfer. Since the heat is absorbed by evaporation rather by an increase in temperature as in the case of molten salt, the recirculation flow rate of the cooling fluid does not play an important role as

long as a quantity of liquid at least equal to the quantity that must be evaporated for the required dissipation of heat is supplied to each cooling tube.

When the recirculated cooling fluid is distributed over the individual cooling tubes, the behavior of the fluid that will be described below may present problems:

Due to the different amount of cooling fluid to be evaporated in the cooling tubes of different reaction zones, the pressure losses that develop inside the cooling tubes differ, with a high pressure loss developing in zones of high heat transfer with high vapor generation and with a low pressure loss developing in zones of low heat transfer with low vapor generation. When all cooling tubes on the coolant side are disposed parallel to one another, the flow through the tubes with high vapor generation is lower than in tubes with low vapor generation. For this method, however, it is better for the flow through tubes with high vapor generation to be preferably higher than in tubes with low vapor generation. To achieve this objective, flow restrictors with different flow resistances on the inlet or outlet side of each individual tube can be used. To this end, the flow resistance of the flow restrictors is adjusted to the expected generation of vapor in each tube.

Another advantage of using a vaporizable cooling fluid is that after separation of the liquid phase in the vapor drum, the vapor of the cooling fluid that developed in the cooling tubes can be used in other parts of the PA plant. Of special advantage in this context is the high temperature level of the available vapor. As a result, it is easily possible to replace complex and expensive heating equipment, e.g., an electric heating system or a separate fired heat transfer system, which must be designed for temperatures of at least 300°C. This leads to a considerable reduction of investment and operating costs. /8

It may be useful for the method to operate the individual reaction zones at different temperatures. This may be accomplished, e.g., by connecting the reactor to two or more separate cooling systems. The cooling fluid can have the same or a different material composition.

The feedstock mixture can flow either substantially horizontally or substantially vertically (from the top to the bottom or vice versa) through the cooling tube-type reactor. When the reactor is designed for vertical flow, space is saved and the cooling tubes may be designed as U-tubes without a welded joint with respect to the gas space and be welded into the reactor in such a manner that if the welded joint were to leak, cooling fluid is unable to enter into the gas space.

The cooling tube-type reactor can be used alone or connected in series to one or more other reactors that can be disposed upstream and/or downstream of the cooling reactor. In this context, the multi-tube reactor, the fluidized-bed reactor and the liquid-phase reactor will be mentioned solely by way of example.

Embodiments of the process using a cooling tube-type reactor will be explained with reference to the drawing. Although reference is made to the production of PA, it is possible to produce another substance in an analogous manner.

In the drawing

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Figure 1 shows a flow diagram of the process,

Figure 2 shows a longitudinal section of a cooling tube portion in an enlarged representation,

Figure 3 shows a flow diagram of the process with two separate cooling circuits, and

Figure 4 shows a flow diagram of the process with two reactors.

As shown in Figure 1, the vaporous feedstock mixture that contains orthoxylene or naphthalene and molecular oxygen flows through the upper inlet (2) into the cooling tube-type reactor (1). Inside the reactor, at least 40 wt% of the catalyst (5) is disposed as a coating on the outside of numerous cooling tubes (3), also cf. Figures 3 and 4, onto which ring-shaped fins (4) are welded. Figure 2 shows a tube section, the outside of which is coated with the catalyst coating (5) as indicated by dots.

The reactor (1) of Figure 1 has a preheating zone (6), a main reaction zone (7) and a secondary reaction zone (8), each having slightly different temperatures. Through these zones, the feedstock mixture flows downward and past the catalyst-coated tubes. The vaporous product mixture that contains PA vapor exits the reactor (1) through the outlet (10) and is subsequently cooled in a manner known from the prior art (not shown) (e.g., U.S. Pat. No. 4,592,412).

All zones (6,7,8) have bundles of finned tubes (3) through which cooling fluid flows. In addition to the cooled tubes, there are uncooled metal or non-metal surfaces (9) coated with catalyst coating, which surfaces are mainly part of the secondary reaction zone (8). The bundles of the preheating zone (6) in the inlet region of the reactor (1), on the other hand, can optionally be catalytically coated or they can be uncoated.

The individual bundles of tubes can either be built into the reactor in such a manner that they can be pulled out or they can be welded to the reactor. The various parts of a bundle of tubes are, for example, undetachably connected to each other, and the catalyst coating is applied to the finished bundle, which is not specifically shown in the drawing. The largest part of the length of the cooling tubes extends /10 horizontally inside the reactor corresponding to a horizontal U-shape of the tubes, in which case welded areas are avoided in the gas space. As a result, the problem of thermal stresses caused by thermal expansion is largely avoided.

The cooling fluid in the form of a liquid exits from line (11) of a vapor drum (13) and is distributed by means of the pump (12) via the lines (11a to 11e) to the various tubes. The cooling fluid in the form of a liquid enters the cooling tubes (3) preferably from the bottom and partly evaporates in the cooling tubes, thus making it possible for the heat of evaporation to be used for cooling. A suitable cooling fluid for use in this process is Diphyl, a synthetic heat transfer oil. Partly evaporated cooling fluid exits from the tubes (3) through lines (14a to 14e) and flows through line (14) to the vapor drum (13).

In line (15), cooling fluid vapor issues through the throttle valve (16) and is cooled in a heat exchanger (17). In line (18), the condensate formed flows to an intermediate tank (19) and is subsequently recirculated into the vapor drum (13) via the pump (20) and line (21). A pressure control system (22) monitors the pressure in the vapor drum (13) and keeps it approximately constant at a predetermined value, with the throttle valve (16) being actuated as required via the signal line (23). By means of the approximately constant pressure, the temperature of the liquid cooling fluid in line (11) and of the partly evaporated cooling fluid in the cooling tubes (3) is kept at the desired temperature which, when Diphyl is used as cooling fluid, is usually in a range from approximately 300 to 400°C.

When the operation is carried out with two reactors, e.g., when a plant is expanded, the second reactor is disposed either upstream of the inlet (2) or downstream of the outlet (10) of the cooling tube-type reactor (1).

Figure 3 shows the same reactor that is seen in Figure 1, except that it is connected to two separate cooling circuits. Thus, it is possible to operate the secondary reaction zone (8) of the reactor at temperatures that are independent of the temperatures of the main reaction zone (7). In this case, as shown in Figure 1, the cooling tubes (3) of the main reaction zone (7) are supplied with cooling fluid via lines (11c to 11e) from the vapor drum (13). The cooling tubes (3) of the secondary reaction zone (8), on the other hand, contain cooling fluid from the second vapor drum (26), with the temperatures of the cooling fluids in the two vapor drums (13 and 26) possibly being different. Partly evaporated as well as /11 unevaporated cooling fluid flows through lines (27a, 27b) into the collecting line (27) and from there into the vapor drum (26). The pressurization of the vapor drums (13 and 26) and the condensation and recirculation of the condensed cooling fluid take place using the same procedure as already described for Figure 1.

According to another embodiment of the invention, part of the generated heat of reaction is used to heat systems of the PA plant that are located outside the reactor region, for example, in the thermal pretreatment and in the distillation of the crude PA. To this end, cooling fluid can optionally be withdrawn in the form of vapor via line (15a) or in the form of a liquid via line (11f) and be transported to the systems that are to be heated. The condensed vapor or the cooled liquid is subsequently recirculated into the reactor cooling circuit via line (18 a).

Figure 4 shows a cooling tube-type reactor (1) similar to the one of Figure 1, but without the preheating zone (6) and the main reaction zone (7). Upstream of this cooling tube-type reactor, a second reactor is disposed, in this case a multi-tube reactor of conventional type, in which the feed gas is preheated and the main reaction takes place. This second reactor will hereinafter be referred to as tubular reactor both in the description of Figure 4 and in Example 2.

The vaporous feedstock mixture that contains orthoxylene or naphthalene and molecular oxygen flows through the inlet (32) into this tubular reactor (31). In the tubular reactor (31), the catalyst (34) in granular form is disposed inside numerous indirectly cooled tubes (33).

For dissipating heat and for controlling the temperature, a cooling fluid is used, for example, a molten salt that enters the lower part of the tubular reactor (31) via line (35), flows through this tubular reactor on the outside of the tubes and exits the reactor at the upper end via line (36). Since the system for transporting and re-cooling the cooling fluid is generally known, it is not necessary at this time to explain and describe it in detail.

The tubular reactor (31) comprises a preheating zone (6) and a main reaction zone (7). Through these zones, the feedstock mixture flows downward inside the tubes (33) that are filled with the catalyst (34). The vaporous product mixture, which contains PA vapor as well as considerable quantities of unreacted

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feedstock and possible intermediate products, exits the tubular reactor (31) through the outlet (37) and flows through the line (38) to the cooling tube-type reactor (1) for further reaction.

Through the upper inlet (2), the vaporous mixture from the tubular reactor (31) flows into the reactor (1). In the reactor (1), the catalyst is at least partly disposed on the outside of numerous cooling tubes (3), as described in conjunction with Figure 1. In contrast to Figure 1, however, the reactor (1) of Figure 4 has only the secondary reaction zone (8) since the preheating zone (6) and the main reaction zone (7) are already disposed in the tubular reactor (31). The vaporous product mixture that contains PA vapor but practically no unreacted feedstock or possible intermediate products exits through the outlet (10) the reactor (1) and is subsequently cooled in a manner known from the prior art (not shown) (e.g., U.S. Pat. No. 4,592,412).

The dissipation of heat and the temperature control of the reactor (1) of Figure 4 take place in the same manner as described in Figure 1 by means of a partly evaporated cooling fluid.

#### Example 1:

In this case, the method is operated with only one reactor as in Figure 1. The cooling tube-type reactor (1) is designed for an hourly volume flow of air that has been preheated to 180°C in a quantity of 60,000 m<sup>3</sup> under standard conditions, which air is mixed with 6000 kg orthoxylene as feedstock in the form of vapor. The temperature of the gas mixture entering the reactor through the inlet (2) is 150°C. 90% of the orthoxylene used is converted in the main reaction zone (7) and the rest in the secondary reaction zone (8) into the end product, i.e., PA, and into byproducts.

The reactor is vertically disposed, with the gas entering from the top. The reactor has a rectangular shape with a width of 3200 mm and a depth of 3100 mm; the height measures approximately 6 m, which



is the overall height including the gas-side hoods at the inlet and outlet. Inside the reactor, two finned-tube heat exchanger bundles are disposed one beside the other at the same level.

The entering gas mixture first flows through the preheating zone (6), which consists of a pair of parallel U-shaped finned-tube heat exchanger bundles made of steel, and along its path is heated to 250°C. Liquid Diphyl, which enters the tubes (11e) at a temperature of 370°C, flows through the tubes (3) of the bundles and on its path through the tubes to the outlet (14e) is cooled to approximately 320°C

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The preheated feedstock gas subsequently flows through the main reaction zone (7) that consists of 15 pairs of parallel arranged U-shaped finned-tube heat exchanger bundles, the outer surface of which is coated with a catalytic substance. The catalytic substance consists predominantly of vanadium pentoxide and titanium dioxide. On contact of the gas mixture with the catalyst, the orthoxylene contained therein reacts with oxygen that is also present to form PA and other byproducts, in the course of which reaction heat is released. Diphyl flows through the inside of the tubes (3) and, due to evaporation absorbs the heat of reaction, which makes it possible to maintain the catalyst temperature constant. Each bundle is fitted with 21 parallel U-tubes (3). The U-shaped finned tubes have an outside diameter of 30 mm and a wall thickness of 2 mm; the straight length of the tube is 3.0 m. The fins have an outside diameter of 60 mm and a thickness of 0.5 mm. The material of the fins and inner tubes is copper. The spacing between two adjacent fins is 1.5 mm so that each U-tube has 3000 fins. The catalytically coated surface area of the fins of each bundle measures 273.1 m<sup>2</sup>.

The heat that will be dissipated by all finned tubes of the main reaction zone (7) in the case of an expected 90% conversion of the orthoxylene used is approximately 22.600 kW. Because of the temperature differences required for the heat transfer inside the wall of the tube and in the fin as well as between wall of the tube and the evaporating Diphyl, the temperature increases from the inside of the tube in the direction of the edge of the fin. In this example, the temperature for the evaporating liquid is

370°C, for the fin at the fin base 374°C, and at the edge of the fin 384°C. By favorably configuring each pair of bundles, each of which is offset by 180°C [sic; °] with respect to the one upstream and downstream of the gas stream, the overall height of the entire main reaction zone is 1950 mm.

The reaction gas mixture subsequently flows through the secondary reaction zone (8), in which the residual orthoxylene is converted. The generated heat of reaction is approximately 2500 kW. The secondary reaction zone consists of 20 finned-tube heat exchanger bundles and 10 elements (without cooling) of catalytically coated monolithic ceramic components (9) in the shape of honeycombs. In design, dimensions and configuration, the finned-tube heat exchanger bundles are largely identical to the bundles used for the main reaction zone (7), with the difference that the thickness of the fins in the secondary reaction zone is 1 mm and the bundles are entirely made of steel. As in the main reaction zone, the bundles are offset in pairs. One layer of uncooled elements of monolithic components is disposed downstream of each of the lowermost 5 pairs of bundles. /14

The Diphyl recirculation pump (12) draws in the liquid Diphyl required for the individual reactor zones from a vapor drum (13) that is disposed at a height of 11 m above the pump. It transports, as needed, different quantities of liquid Diphyl to the individual reactor zones, i.e., 100 m<sup>3</sup>/h to the preheating zone, 2000 m<sup>3</sup>/h to the main reaction zone, and 200 m<sup>3</sup>/h to the secondary reaction zone.

The Diphyl that exits from the bundles of the individual reactor zones partly in liquid form and partly in the form of vapor is recirculated back into the vapor drum (13) via a joint collecting line (14). In the vapor drum, the vapor phase is separated from the liquid phase, and the liquid is again available for recirculation. The pressure in the vapor drum is 7.5 bar, which corresponds to a saturated vapor temperature of 370°C. The quantity of Diphyl vapor that is discharged via line (15) is 400,000 kg/h.

The vaporous Diphyl that is discharged from the vapor drum (13) through line (15) is largely reliquefied in several condensers (17), collected in the tank (19), and recirculated into the vapor drum (13) via the pump (20).

In one of the condensers, the heat of condensation is used to generate saturated vapor of 51 bar. In another condenser that is connected in parallel thereto, the saturated vapor thus generated is superheated to a temperature of 330°C and is thus available for driving a vapor turbine. By means of the heat that is transferred per hour by the condensation of 400,000 kg of Diphyl vapor, approximately 37 metric tons of superheated vapor are generated in this manner. /15

For heating the distillation of the crude PA with a heat requirement of 2000 kW, another part of vaporous cooling fluid is withdrawn in an amount of 32,000 kg/h. The cooling fluid condensed in the heat-consuming devices flows through line (18a) back into the coolant system of the reactor.

#### Example 2:

In this case, the method is operated as shown in Figure 4. The two reactors (31) and (1) are designed for an hourly volume flow of carrier gas (preheated ambient air) of 60,000 Sm<sup>3</sup> that is loaded with orthoxylene as feedstock in the vapor state in a quantity of 7200 kg/h. The temperature of the gas mixture that enters the tubular reactor (31) through the inlet (32) is 143°C.

The tubular reactor (31) has 15,000 vertically arranged steel tubes (33) with an inside diameter of 25 mm and a length of 3.4 m. The catalyst (34) inside the tubes has a filling level of 3.1 m and consists of ring-shaped substrate components made of an inert ceramic material with a diameter of 7 mm and a length of 7 mm that are coated with a thin layer of a catalytic material, mainly consisting of vanadium pentoxide.

The gas mixture of preheated air and vaporous orthoxylene that serves as feedstock enters the tubes (33) from the top at a temperature of 144°C. As the gas passes through the upper catalyst-free part of the tubes that measure approximately 150 mm in length and the uppermost 100 mm of the catalyst packing, it is heated in the preheating zone (6) to a reaction temperature of 330°C.

Because of the reaction that subsequently sets in, the gas is further heated and, once the temperature has exceeded the cooling fluid temperature of 350°C, emits heat to the tube wall. At a level of 500 mm below the inlet of the catalyst bed, the gas reaches its maximum temperature of 410°C. (hot spot). Below the hot spot, the gas cools down again and, as it exits the tubes (33), reaches a temperature of 360°C.

Upon contact of the gas mixture used with the catalyst (34) in the main reaction zone (7), the orthoxylene contained therein reacts to form PA and other byproducts, in the course of which reaction heat is released. The reaction conditions are such that an unreacted fraction of approximately 10% of the orthoxylene used exits the tubular reactor (31) together with the reaction gas via line (38).

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The heat to be emitted from the reactor (31) by the cooling fluid in the case of an expected 90% conversion of the orthoxylene used is approximately 18,000 kW.

The cooling tube-type reactor (1) is vertically arranged, as shown in Figure 4, with the gas mixture entering from the top. This reactor has a rectangular shape with a width of 3.2 m and a depth of 3.1 m, and the height is approximately 4 m, which is the overall height including the gas-side hoods at the inlet and outlet. Inside the reactor (1), two finned-tube heat exchanger bundles (3) or two uncooled elements (9) are disposed one beside the other at the same height, as will be described in greater detail below.

In the cooling tube-type reactor (1), the reaction gas from the tubular reactor (31) flows around the bundles (3) and the uncooled elements (9). The surface of both the bundles and the elements is coated with a catalytic material. As the gas mixture comes into contact with the catalyst, the orthoxylene contained therein and the intermediate products that formed in the tubular reactor (31) react with

oxygen that is also present to form PA and other byproducts, in the course of which reaction heat is released. The heat of reaction generated in the reactor (1) is approximately 3000 kW.

The reactor (1) comprises 20 finned-tube heat exchanger bundles (3) and 10 elements (9) that are formed of monolithic ceramic components in the shape of honeycombs without cooling. The outer surface areas of the U-shaped finned tubes (3) of the bundles and the inside surfaces of the honeycombs of the monolithic components of the elements (9) are coated with a catalytic coating. In both cases, the catalytic material consists mainly of vanadium pentoxide.

The bundles are arranged in pairs. One layer of uncooled elements (9) of monolithic components that are also arranged in pairs, is disposed downstream of each of the bottommost 5 pairs of bundles.

Diphenyl, which absorbs the reaction heat by evaporation, flows through the inside of the tubes (3) of the bundles, thereby making it possible to maintain the catalyst temperature constant. /17

Each bundle is fitted with 21 parallel U-tubes (3). The U-shaped finned tubes have an outside diameter of 30 mm and a wall thickness of 2 mm; the straight tube length is 3.0 m. The fins have an outside diameter of 60 mm and a thickness of 1 mm. The material of which the fins and inner tubes are made is steel. The spacing between two adjacent fins is 1.5 mm so that each U-tube has 2400 fins. The catalytically coated fin surface of each bundle measures  $218.5 \text{ m}^2$ .

Due to the temperature differences required for the heat transfer inside the tube wall and in the fin as well as between wall of the tube and the Diphenyl that is to be evaporated, the temperature increases from the inside of the tube in the direction of the edge of the fin. In this example, the temperature for the evaporating liquid is  $350^\circ\text{C}$ , for the fin at the base of the fin  $350.5^\circ\text{C}$ , and at the edge of the fin  $360^\circ\text{C}$ .

The uncooled elements consist of catalytically coated monolithic elements with an edge length of  $150 \times 150 \times 150 \text{ mm}$  in the shape of honeycombs. Since the released heat of reaction is not dissipated in the honeycombs, the gas, when flowing through a monolithic element, is heated by 1 to  $5^\circ\text{C}$ . This

elevated temperature decreases as the gas flows through the next cooled bundle by releasing heat along the finned tubes.

By favorably configuring each pair of bundles, each of which is offset by  $180^\circ$  with respect to the one upstream and downstream of the gas stream, the overall height of the entire reaction zone (8) is 2.1 m.

The liquid Diphyl required for cooling the reactor tubes is drawn in by the Diphyl recirculation pump (12) from a vapor drum (13) that is disposed at a height of 10 m above the pump. It delivers  $250 \text{ m}^3/\text{h}$ .

The Diphyl that exits from the bundles via lines (14a) and (14b) partly in liquid form and partly in the form of vapor is recirculated to the vapor drum (13) via a joint collecting line (14). In the vapor /18 drum, the vapor phase is separated from the liquid phase, and the liquid is again available for recirculation. By means of a throttle valve (16) in the vapor outlet line (15), which is actuated by a pressure controller (22) via a pulse line (23), the pressure in the vapor drum is maintained at a constant pressure of 5.6 bar, which corresponds to the saturated vapor temperature of  $350^\circ\text{C}$ . The quantity of Diphyl vapor that is discharged via line (15) is approximately  $45,000 \text{ kg/h}$ . The delivery pressure of the pump for overcoming the flow resistances in the bundles with the built-in throttle elements and in the tube lines that supply and discharge the Diphyl is 1 bar.

The vaporous Diphyl that is discharged from the vapor drum (13) through line (15) is largely reliquefied in a condenser (17), collected in the tank (19), and recirculated into the vapor drum (13) via the pump (20). The heat of condensation is used to generate saturated vapor of 51 bar. By means of the heat that is transferred by the condensation of Diphyl vapor in a quantity of  $45,000 \text{ kg/h}$ , 4 metric tons of vapor per hour are generated.

1. A method for catalytically generating organic substances by partial oxidation of an organic feedstock material in the presence of molecular oxygen at temperatures in a range from 200 to 500°C in one or a plurality of series-connected reactors containing a catalyst for generating a gaseous product mixture, characterized in that at least one reactor is a cooling tube-type reactor with cooling tubes through which a cooling fluid is flowing, wherein 40 to 100 wt% of the total quantity of the catalyst of the cooling tube-type reactor is disposed as a coating on the outside of the cooling tubes and the feedstock mixture containing the feedstock substance and the molecular oxygen comes into contact with the catalyst coatings.
2. The method according to Claim 1, characterized in that inside the cooling tube-type reactor, at least half of the cooling tubes are finned tubes with fins projecting on the outside, said fins being at least partly coated with catalyst.
3. The method according to Claim 2, characterized in that at least 10 wt% of the total quantity of catalyst of the cooling tube-type reactor is applied in the form of a coating to the fins.
4. The method according to Claim 1 or one of the other preceding claims, characterized in that 5 to 40 wt% of the total quantity of catalyst of the cooling tube-type reactor is disposed on uncooled metal surfaces.
5. The method according to Claim 1 or one of the other preceding claims, characterized in that the feedstock mixture flows substantially vertically through the cooling tube-type reactor and in that the cooling tubes are in part arranged horizontally inside the reactor.
6. The method according to one of Claims 1-5, characterized in that the cooling fluid enters the cooling tubes of the cooling tube-type reactor in the form of a liquid and partly evaporates in the cooling tubes.

7. The method according to Claim 1 or one of the other preceding claims, characterized in that the catalyst coatings inside the cooling tube-type reactor have layer thicknesses in the range from 0.05-5 mm.

8. The method according to Claim 1 or one of the other preceding claims, characterized in that several cooling systems are available, which transport cooling fluid to and withdraw cooling fluid from the cooling tubes of the cooling tube-type reactor. /20

9. The method according to Claim 1 or one of the other preceding claims, characterized in that one of the substances, phthalic anhydride (PA), maleic anhydride, acrylic acid, acetic acid or anthraquinone is at least partially produced in the cooling tube-type reactor.

10. The method according to Claim 1 or one of the other preceding claims, characterized in that the cooling tube-type reactor interacts with at least one other reactor that is disposed upstream or downstream of the cooling reactor.

11. The method according to Claim 10, characterized in that the other reactor is a multi-tube reactor with a catalyst bed in the tubes, a fluidized-bed reactor or a liquid-phase reactor.





Fig. 3



